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THE SYNTHESIS OF UNSATURATED FLUOROCARBONS

Supported in part by Wright Air Development Division
U. S. Air Force: MIPR 339(616)-5701

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Between

The Office of the Quartermaster General
and

The University of Florida

Quarterly Report 45: June 13, 1962-September 13, 1962

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I. INTRODUCTION

The purpose of this project is to conduct the necessary research for the preparation of unsaturated organic compounds containing fluorine and, when synthetic methods have been developed, to prepare various fluoro-olefins which may give elastomers which are oil and fuel resistant and which retain their elasticity at low temperatures.

It is estimated that 95% of the work has been completed to date and that 95% of the estimated costs have been incurred to date.

This research is authorized under Contract Number DA-19-129-QM-500 and is a further continuation of the work initiated under DA-44-109-QM-522 and continued under DA-44-109-QM-1469. The Wright Air Development Center has contributed funds for the operation of the project in part since September 13, 1956 under MIPR 33(616)-5701.

This is the 28th quarterly report under the contract but the 45rd since the project was initiated in 1951. The period covered is from June 13, 1962 through September 13, 1962.

II. SUMMARY OF CURRENT PROGRESS

A study has been made to develop the best preparative method for nitroso compounds by adding nitrosyl chloride to a fluoroolefin in the presence of $AlCl_3$ and dimethylformide in solution.

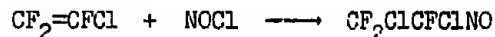
The gas phase reaction of nitrosyl chloride with olefins in sunlight has been investigated and nitroso compounds obtained.

A number of fluoroalkylnitroso compounds have been reacted with butadienes to give oxazines. An attempt to dehalogenate a compound containing chlorine

atoms on adjacent carbon atoms of the side chain apparently did not give the fluorovinylloxazine.

III. DISCUSSION

Some preliminary experiments have indicated that it might be possible to reduce a nitro compound such as $\text{CF}_2\text{ClCFClNO}_2$ to the corresponding nitroso compound. A supply of nitro compound was needed for further study, and it was decided that the best method for preparing nitro compounds for this study was by oxidation of the corresponding nitroso derivative. The preferred method of preparation of nitroso compounds is by the reaction



Consequently some attention was given to establishing conditions which would give maximum yields with a minimum of operating difficulties.

In each case dimethylformide was used as solvent, aluminum chloride was used as catalyst and nitrosyl chloride and chlorotrifluoroethylene as the reagents. It had been found earlier (QR 39, March 13, 1961) that these reagents gave appreciable amounts of nitroso compound.

One set of conditions involved the use of a pressure vessel charged with olefin and nitrosyl chloride. After 3 hours time, the gaseous products were removed by pumping and fresh nitrosyl chloride and chlorotrifluoroethylene added; this operation was repeated several times. Since the yield of nitroso compound was low and appreciable quantities of by-products were formed, it was concluded that this set of conditions was not suited to the production of the desired product.

A better method was found by introducing a mixture of olefin and nitrosyl chloride at the bottom of a vertical tube containing the solvent and catalyst

and collecting the product as it was cooled from the tube.

However, the best conditions for the preparation of batches of half to one pound was found to be as follows:

A 3-neck flask was fitted with stirrer, gas inlet tube and Dry-Ice reflux condenser. The flask was charged with dimethylformamide and aluminum chloride and about 0.2 to 0.3 moles each of nitrosyl chloride and olefin. Heating was begun and the blue vapor removed from the column head as it formed. When evolution of the nitroso compound stopped, fresh portions of nitrosyl chloride and chlorotrifluoroethylene were added and the operation continued. Using such a procedure, a 1/4 lb batch of $\text{CF}_2\text{ClCFClNO}$ was obtained in 56% conversion.

A study was also made of the reaction of nitrosyl chloride with certain fluoroolefins. Perfluoro-2-butene reacted in the gas phase in sunlight with nitrosyl chloride to give as the chief product a small amount of 2-nitroso-3-chloroperfluorobutane. Uns-dichlorodifluoroethylene reacted more rapidly to give a product tentatively identified as $\text{CF}_2\text{ClCCl}_2\text{NO}$ or $\text{CCl}_3\text{CF}_2\text{NO}$.

Reaction between perfluoroallyl chloride and NOCl also took place rapidly in the gas phase in bright sunlight to give a blue colored gas. A crude separation by evaporation in a vacuum line allowed the separation of chlorinated product and nitroso compound. The latter has not been identified but the chlorinated products were shown by NMR analysis to consist of $\text{CF}_2\text{ClCFClCF}_2\text{Cl}$ and $\text{CF}_3\text{-CCl}_2\text{CF}_2\text{Cl}$. Presumably the latter arose from $\text{CF}_3\text{CCl=CF}_2$ present in the perfluoroallyl chloride.

Apparently the reaction of $\text{CF}_2=\text{CHCF}_2\text{Br}$ in complex and does not lead to the ready formation of the desired $\text{CF}_2=\text{CHCF}_2\text{NO}$. Perfluorocyclobutene is also unreactive as little evidence of reaction was noted even after irradiation with sunlight for 18 hours.

The reaction of perfluoroacrylonitrile with nitrosyl chloride would be

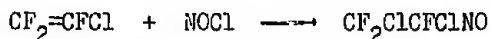
The nitroso compounds employed were $\text{CF}_2\text{ClCFClNO}$, $\text{CF}_3\text{CF}(\text{NO})\text{CF}_2\text{Cl}$ and $\text{CF}_2=\text{CFCF}_2\text{NO}$. The latter material reacted explosively with butadiene.

It was of some interest to determine if halogen atoms could be removed from adjacent carbon atoms in a compound such as $\text{ClCF}_2-\text{CFClnO}\text{CF}_2\text{CF=CHCH}_2$. Such information would be useful in attempting to form $\text{CF}_2=\text{CF}-$ groups in nitroso polymers containing the $\text{CF}_2\text{ClCFCl}-$ group. The oxazine was treated with zinc in 1-propanol. Infrared analysis indicated the presence of the $\text{CF}_2=\text{CF}-$ group as absorption at 5.6μ was observed. However, NMR analysis does not support such a structure and it is entirely possible that the peak at 5.6μ is due to a carbonyl group.

IV. EXPERIMENTAL

A Study of the Reaction of Chlorotrifluoroethylene with Nitrosyl Chloride
to develop Preparative Method

The reaction



was run under three sets of conditions to determine which was the best for the preparation of large samples of nitroso compounds.

A 1.4 liter autoclave was charged with 300 ml. of dimethylformamide, 0.25 mole aluminum chloride, and 1 mole each of olefin and nitrosyl chloride. After rocking about 3 hours at room temperature the products were pumped out, and more olefin and nitrosyl chloride were added to the residue in the autoclave. This process was repeated several times. The yields of nitroso material were low, and considerable chlorinated and nitro products were also obtained. It was decided that these conditions were unsatisfactory for laboratory preparations.

A 2 inch vertical tube was filled to a height of 3 feet with a mixture of dimethylformamide and aluminum chloride. (Acetic acid was also tried as a solvent but did not work). Nitrosyl chloride and olefin were passed through, and exiting vapors were bubbled through a column of water. Nitroso product was obtained in at least 95% purity, but it was observed that the tube had to be heated to about 60° for the product to be collected. At lower temperatures the product accumulated in the tube and increased the volume of the liquid. It was decided that this method was useful in preparing large quantities of nitroso material.

For the preparation of up to about a pound of nitroso material, the following method was considered the most convenient. A 500 ml., 3-N flask was

equipped with a heating mantle, a mechanical stirrer, a gas inlet tube, and a low temperature distillation head at -78° . About 0.24 to 0.33 moles each of nitrosyl chloride and olefin was bubbled into 150 ml. of dimethylformamide and 23 g. of aluminum chloride. The mixture was heated with stirring. When the condensing vapors became dark blue (about 15 min.), the product was slowly drawn off. [Note: Heating is necessary because the refluxing olefin quickly cools the pot. Once the reaction gets started, it appears to be exothermic]. When no more product was collected, another 0.25-0.33 mole portion each of nitrosyl chloride and olefin was added, and the process repeated. In this case, 102 g. of nitroso material was prepared in 56% conversion.

The Reaction of Nitrosyl Chloride with Various Fluoroolefins

A. With perfluoro-2-butene. A 2 liter evacuated flask was charged with 325 mm. olefin and 325 mm. of nitrosyl chloride. After irradiation in bright sunlight for 2 hours, the gases were still brown; after 5 hours they had become yellow-green. The products were condensed and passed through a preparative scale VPC. Some olefin was recovered. The main product was 1.5 g. of 2-nitroso-3-chlorooctafluorobutane. This was identical to previous material prepared in an aluminum chloride-dimethylformamide system.

B. With 1,1-dichlorodifluoroethylene. The reaction was carried out as described above. After 1.5 hours of irradiation in bright sunlight, the gases had become brilliant blue. The product was purified by VPC, and its molecular weight was determined as 197 (calc'd. for $C_2Cl_2F_2NO$: 198.5). The infrared spectrum indicated the presence of the nitroso group, but NMR analysis could not distinguish between the structures CF_2ClCCl_2NO and CCl_3CF_2NO . Since only one of these is present, it is most likely to be the first.

C. With 3-chloropentafluoropropene. The reaction was carried out as described above. The gases became blue after about 1.5 hours of sunlight

irradiation. The products were partially separated by vacuum line fractionation. NMR analysis of the chlorinated material obtained indicated it to be a mixture of about 70% $\text{CF}_3\text{-CCl}_2\text{-CF}_2\text{Cl}$ and $\text{CF}_2\text{Cl-CFCl-CF}_2\text{Cl}$. The nitroso compound has not yet been purified.

D. With $\text{CF}_2=\text{CHCF}_2\text{Br}$. The reaction was carried out as described above. After 3.5 hours of irradiation, the gases had become greenish yellow. Vacuum line separation yielded 0.5 g. of a green product which has not been further purified. NMR can only indicate a mixture.

E. With perfluorocyclobutene. The dichloride was reacted with zinc to obtain 8 g. of the olefin in 67% yield.

The olefin was reacted with nitrosyl chloride as described above, but the gases remained brown even after 18 hours of irradiation. This material has been condensed and stored at -78° but has not yet been purified since no nitroso product was obtained.

The Reaction of Perfluoroacrylonitrile with Nitrosyl Chloride

A Pyrex tube containing 2.0 ml. of nitrosyl chloride, 2.8 ml. of perfluoroacrylonitrile, and about a gram of aluminum chloride was shaken five hours in the dark with no apparent reaction. The tube was then put in bright sunlight and exploded after 5 to 6 hours.

A one liter flask was evacuated and filled with equal amounts of the two gases to a total pressure of 650 mmHg. At the end of 2.5 hours of sunlight irradiation the gaseous material had become grass-green. When the flask had been pumped out, a white film remained on the walls and peeled off in spots. The material condensed out of the flask was passed through the preparative VPC.

One fraction was identified by NMR analysis to be the expected chlorinated

material, $\text{CF}_2\text{ClCFClCN}$. Its IR spectrum was consistent with this structure. The IR spectrum of the second fraction had a strong peak at 6.2μ indicating a nitro group and a peak at 4.4μ characteristic of the cyano group. Analysis by NMR showed the compound to be $\text{CF}_2\text{NO}_2\text{CFClCN}$. A 20-25% impurity was present according to NMR but it did not appear according to gas chromatographic analysis. According to NMR this impurity is $\text{CF}_2\text{ClCFClNO}_2$.

The Reaction of Nitroso Compounds with Butadienes

The reactions were carried out in sealed tubes as described in an earlier report.

A. 1-Nitroso-1,2-dichlorotrifluoroethane and 1,1,2-trifluorobutadiene.

Fourteen grams (0.077 mole) of nitroso compound was reacted with 6.5 g. (0.060 mole) of the diene to obtain 8.7 g. (0.03 mole, 50%) of the oxazine, $n_D^{21}=1.4014$ [D. E. O'Connor reported $n_D^{19}=1.4016$]. A polymeric material was also obtained which decomposed on attempted distillation.

B. 2-Nitroso-1-chlorohexfluoropropane plus 1,1,2-trifluorobutadiene.

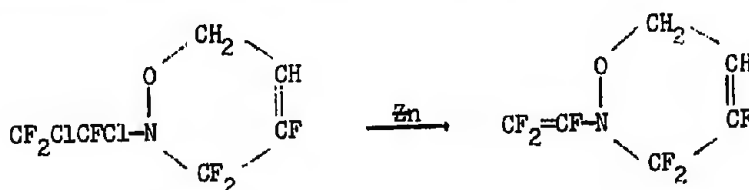
Five grams of the nitroso compound (0.023 mole) reacted with 4.6 g. of the diene (0.0425 mole) to yield 4.3 g. (0.0153 mole, 58%) of the oxazine, b.p. $52^\circ/5\text{mm}$. $n_D^{21}=1.3676$. A polymeric gum was also obtained which decomposed on attempted distillation.

C. 2-Nitroso-1-chlorohexafluoropropane plus butadiene. Five grams of the nitroso compound reacted with 2 g. of the diene to yield 5.4 g. (87%) of the oxazine, b.p. $51^\circ/9\text{mm}$., $n_D^{21}=1.3916$.

D. 1-Nitrosoentafluoropropene-2 plus 1,1,2-trifluorobutadiene. Two and one half grams of the nitroso material (0.014 mole) violently reacted with 0.014 mole of the diene. Fragments of the glass tube seemed to be covered with black soot. This jarring, charring reaction will be attempted again if more of the nitroso material becomes available.

The Reaction of $\text{CF}_2\text{ClCFCl-N-CF}_2\text{CF=CHCH}_2\text{O}$ with Zinc

The above material (2.90 g., 0.01 mole) was refluxed for 2.5 hours with 15 ml. of 1-propanol, 2 g. of zinc dust, and a pinch of zinc chloride. No low boiling material was collected. The mixture was filtered, and unreacted zinc was washed with a little propanol. After removal of the solvent, the residue was distilled at reduced pressure. Only 0.45 g. of material was obtained, b.p. $55^\circ/2\text{mm}$, $n_D^{22}=1.4297$. (Note: $n_D^{19}=1.4016$ for starting material). The infrared spectrum of the product looked like what was anticipated if dichlorination had occurred. A band at 13.9μ in the starting material was no longer present in the product, and the product showed a strong new band at 5.6μ which did not appear in the IR of the starting material. It thus was assumed that the following reaction occurred:



Unfortunately, the NMR spectrum of the product disagrees and suggests that a rearrangement of some sort has occurred. Furthermore, the perfluorovinyl group is not present, so the IR band at 5.6μ must be caused by a carbonyl. Both IR and NMR agree that the group $-\text{CH=CF}-$ is probably still intact.

V. FUTURE WORK

Attempts will be accelerated to prepare functional group nitroso compounds. The reaction of $\text{CF}_2=\text{CFCOF}$ and NOCl will be attempted. Efforts will also be made to prepare compounds such as $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Si}\equiv$ to determine if such substances will react with NOCl to give nitrososilanes.

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